Surface transport of 2,4-D from small turf plots: observations compared with GLEAMS and PRZM-2 model simulations

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Abstract: A three-year field study was conducted using twelve 7.4 × 3.7 m plots and simulated rainfall to investigate pesticide run-off following application to a golf course fairway. The plots were sprigged with 'Tifway 419' bermudagrass (*Cynodon dactylon* × C *transvaalensis*). The dimethylamine salt of 2,4-D [(2,4-dichlorophenoxy)acetic acid] was applied as foliar sprays at a rate of 2.24 kg AI ha^{-1}. Simulated rainfall was applied at an intensity of 29 mm h^{-1} one day before and 1, 2, 4, and 8 days after the pesticide applications for 0.92, 1.75. 1.75, 0.92, and 0.92 h, respectively. Water run-off was measured using a tipping-bucket apparatus and sub-samples were analyzed for pesticide residues. Data collected from the study were also compared with the GLEAMS and PRZM-2 model simulations for surface water and 2,4-D run-off. Mass and concentration of 2,4-D in run-off decreased rapidly, with 74.5% of the total run-off of 2,4-D occurring in the first run-off event after treatment. When calibrated to the site-specific characteristics, the GLEAMS and the PRZM-2 models adequately simulated the average of surface water run-off over all plots, with normalized root mean square error (NRMSE) and coefficient of determination for linear regression (R^2) being 22.8% and 0.917 for GLEAMS, and 23.7% and 0.879 for PRZM-2, respectively. However, both GLEAMS (NRMSE = 82.1%, R^2 = 0.776) and PRZM-2 (NRMSE = 125.8%, R^2 = 0.513) less accurately simulated 2,4-D concentrations in run-off.

Keywords: run-off; golf courses; pesticides; GLEAMS; PRZM-2; grassland

1 INTRODUCTION

Surface transport of pesticides from urban systems such as golf courses is an ecological and human health concern because such systems are usually adjacent to residential areas and the systems are under intensive management, with high inputs of pesticides and fertilizers. Wauchope[1] showed that, for agricultural uses, significant amounts of pesticides could be lost via surface run-off it the water run-off volume was relatively large and occurred shortly after pesticide application. A severe scenario of rainfall run-off and pesticide application timing such as this does not often occur for agricultural crops, but there is a greater possibility for it to occur in golf courses because of intensive use of pesticides, fertilizers, and irrigation. Therefore, characterizing surface run-off pesticides from golf courses under severe scenarios is needed. Large-scale field studies on pesticide run-off are expensive and difficult to conduct and are also dependent on occurrences of natural rainfall. These limitations have motivated use of field plots and simulated rainfall as a new approach[2] to study pesticide run-off following application.

Simulation models such as GLEAMS[3] and PRZM-2[4] predict water movement and pesticide transport by integrating major processes that operate on water and pesticides. These two models have been widely used to study the influence of various management practices on water quality in agricultural systems to find the best management practice. However, such applications to urban systems such as golf courses are relatively new. Similarities in pesticide fate between urban and agricultural systems suggest that simulation models developed for agricultural systems could be adopted for urban systems, although the dissimilarities would require appropriate adjustments in model structure and parameterization.

Cohen *et al*[5] compared PRZM-2 predictions with measured concentrations in ground water for five pesticides, including 2,4-D, from four golf courses on Cape Cod and found that the model reasonably simulated the pesticide concentrations in ground

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Contract/grant sponsor: US Golf Association.
Contract/grant sponsor: USDA Cooperative Research Service.
(*Received 1 June 1998; revised version received 25 September 1998; accepted 3 December 1998*)

water. Cohen et al[6] also used the SWRRBWQ model to guide pesticide selections for a proposed golf course in Hawaii by comparing model-predicted concentrations in run-off with the acute aquatic toxicity criteria set up by the US Environmental Protection Agency. Smith and Tillotson[7] applied the GLEAMS model for leaching predictions of 2,4-D from a lysimeter with simulated golf course greens and found that the model greatly overestimated leaching of the pesticide.

While these studies focused on pesticide leaching and demonstrated mixed success and failure in applying simulation models developed for agricultural systems to golf courses, we sought to determine how effectively these models could simulate pesticide run-off. Evaluations of the models for run-off simulations are important because partitioning of rainfall between run-off and infiltration is the first step to accurate prediction of chemical transport. The significant amount of surface run-off generated in the Piedmont Regions of Georgia also requires that simulation models be tested for run-off predictions as well as for leaching predictions.

In 1996 Smith and Bridges[8,9] summarized run-off losses of dicamba, 2,4-D and mecoprop for 1994 from a rainfall simulation experiment in which the herbicides were applied to plots simulating golf fairways and subjected to severe rainfall. In this study, we report more detailed run-off loss of 2,4-D from that experiment including run-off from 1995 and 1996 and compare three years of 2,4-D run-off data with GLEAMS and PRZM-2 model predictions.

2 MODEL DESCRIPTION

The GLEAMS model estimates surface water run-off based on the Soil Conservation Service (SCS) curve number run-off model,[10] driven by daily rainfall, with modifications that relate run-off curve number to daily soil water content in the root zone.[11] The PRZM-2 model also uses the curve number run-off model, but PRZM-2 relates daily run-off curve number to soil moisture limits in the surface zone (top 0.3 m).[4] The soil moisture limits are calculated from soil water content in the surface zone and are simplified to match the three antecedent soil moisture conditions based on five-day antecedent rainfall by USDA-SCS.[10] In these associations, a 1-cm difference in soil water storage is assumed among the three soil moisture limits. The amount of pesticide transported via surface run-off is calculated from edge-of-field water run-off volumes, empirical extraction coefficients and sediment concentrations, by assuming linear equilibrium adsorption isotherm and constant mixing depths at the surface. This depth is 10 mm for GLEAMS and the depth of the surface layer for PRZM-2. Decay of pesticides in both models is simulated by the commonly used first-order rate equation.

Both GLEAMS and PRZM-2 route water flow in the soil profile based on characteristic soil properties such as soil water contents at the field capacity (-33 kPa potential), at the wilting point (-1500 kPa potential), and at saturation. In GLEAMS, potential evapotranspiration (ET) is calculated by the modified Penman–Monteith combination equations or by Priestly–Taylor model; actual ET is calculated by the two-stage evaporation model of Ritchie. In PRZM-2, potential ET is calculated by Hamon's formula or from the pan evaporation; actual ET is extracted successively from each soil layer of the root zone based on the potential demands and actual available soil water content. Transpiration starts at crop emergence and increases stepwise until the maximum rooting depth is attained at crop maturity. The crop/turf growth models employed by GLEAMS and PRZM-2 are mechanistic in nature.

3 MATERIALS AND METHODS

3.1 Field experiment and run-off measurements

The field study was conducted continuously from 1994 to 1996 at the Georgia Agricultural Experiment Station in Griffin, Georgia. A summary report on experimental design, run-off collection, pesticide residue analysis, and pesticide run-off load for 1994 was presented by Smith and Bridges.[8,9] Briefly, twelve 7.4×3.7 m plots were constructed with a 5% slope. This slope is considered typical for golf course fairways in the Piedmont Region of Georgia. The soil was a Cecil sandy clay loam (thermic, Typic Hapludult) which had a low to moderate hydraulic conductivity and a flow-restricting layer between the Bt and BC horizons. The plots were separated by landscape timbers with the tip edge 20 mm above the sod to define the plot area from which run-off was collected. A ditch was dug at the downslope of the plots. For each plot, a tipping-bucket collection apparatus with a chemical-collection trough was installed in the ditch for quantifying run-off volume and sub-sampling for analyzing pesticide residues.

The plots were sprigged with 'Tifway 419' bermudagrass (*Cynodon dactylon* (L) Pers $\times$ *C transvaalensis* Burtt-Davy) in May 1993. By August 1993, the plots were completely covered. The plots were mowed twice a week thereafter during the actively growing season (June via October) with the clippings left on the surface. A Wobbler off-center rotary sprinkler rainfall simulator system (Senninger Irrigation, Orlando, FL) was installed with the two irrigation laterals 7.4 m apart and the risers 3.1 m above the sod. Nozzle spacing along the laterals was 3.7 m. The system operated at 138 kPa and was capable of producing 29 mm h^{-1} rainfall uniformly over the plots. The rainfall simulator system was also designed to simulate closely the major characteristics of the natural rainfall at this intensity such as rainfall droplet size and energy impact.[12]

Before pesticide applications, soil samples were taken to a depth of 1.26 m to measure soil properties. Particle size distribution was determined by the hydrometer method.[13] Saturated hydraulic conductivity was determined by the constant head method[14] using undisturbed soil cores (60 mm ID, 90 mm height) which were then for bulk density measurements. Soil organic carbon content was determined by the modified Walkley–Black method.[15] Soil water contents at the field capacity (−33 kPa potential) and at saturation for each soil horizon were obtained from fitting the measured soil water retention data to the Brooks–Corey functions.[16] The soil water retention characteristics were measured at −1.8, −2.9, −6.2, −12.0, −33.3, and −68.4 kPa potentials using undisturbed soil cores. Soil water retention at −1500.0 kPa potential was measured in a high-pressure chamber using loose soil from each soil horizon. We believe that characteristic soil water contents obtained from fitting all the measured data are more realistic and representative than from a single matric potential measurements. The average over five measurements is summarized in Table 1.

The plots were treated with the dimethylamine salt of 2,4-D (2.24 kg AI ha^{-1}) starting 13 June 1994. There was a total of 19 applications during the three years of study. Two application methods were used, foliar application and pressure injection application, which injects the pesticides into the sod/thatch media. These are recommended uses in golf courses, but the high water-solubility of the active ingredient results in high run-off potentials. 2,4-D has been ranked as risky in terms of groundwater contamination potentials.[7] Usually six replications (plots) were used for characterizing 2,4-D run-off. Occasionally, three plots were used while the remaining plots were treated with other pesticides. Selection of a specific treatment date was based on normal management practices and the weather forecasts to allow for at least 72-h period with a low probability of rainfall. Simulated rainfall was applied at an average intensity of 29 mm h^{-1} one day before and 1, 2, 4 and 8 days after the pesticide treatments for 0.92, 1.75, 1.75, 0.92 and 0.92 h, respectively. A rainfall intensity and duration of this magnitude (29 mm h^{-1} for 1.75 h) occur with a return frequency of approximately once per year in the south-eastern US, based on our analysis for 15-min rainfall records from 1985 to 1994. The pre-treatment rainfall was to create a consistent, pre-wetted initial moisture condition. This combination of antecedent soil moisture condition and pesticide and rainfall application timing represents a severe scenario for pesticide run-off. However, it would not be impossible for a golf course to experience such a scenario because of the intensive irrigation, pesticide applications, and the rainfall pattern in the Piedmont Region of the south-eastern US.

Run-off was collected for each plot by a tipping-bucket apparatus and a small but constant number of sub-samples were taken for pesticide residue analysis. Each tipping-bucket apparatus was calibrated before each simulated rainfall. We did not continue to collect samples after the 8th day run-off event because 2,4-D concentration in this run-off event was generally below the analytical detection limits of 0.5 μg $liter^{-1}$. Run-off from natural rainfalls was collected starting in 1996 and analyzed in the same way as that from the simulated rainfalls.

3.2 Parameterizations of GLEAMS and PRZM-2

Daily mean air temperature, solar radiation, and rainfall were obtained from the Georgia Automated Environmental Monitoring Station adjacent to the site. Measured soil particle size distribution, organic carbon content, soil water content at −1500 kPa potential, and saturated hydraulic conductivity were used as model inputs. Soils porosity was calculated from measured soil bulk density by assuming soil particle density of 2.65 Mg m^{-3}. GLEAMS and PRZM-2 require run-off curve numbers (CN) for antecedent moisture condition II (normal condition) (CN_{II}) in order to initiate surface water run-off estimates. The CN is an empirical parameter whose value depends primarily on soil properties, land uses, and antecedent moisture conditions (dry, normal, and wet). Depth to water table and existence of impervious layers can also greatly influence the CN values. Values for CN_{II} have been tabulated for a range of hydrologic soil-cover complexes across the United States.[10] This table, although comprehensive, does not include CN_{II} values for golf

Table 1. Average of measured soil and soil hydraulic properties of Cecil sandy clay loam, Georgia Agricultural Experiment Station, Griffin, Georgia[a,b]

Depth (m)	*Sand* (%)	*Silt* (%)	*Clay* (%)	*OC* (%)	*ρ* Mm^{-3}	K_s^a ($cm\,h^{-1}$)	$\theta_{.33}$ (m^3m^{-3})	θ_{15} (m^3m^{-3})
0.0 to 0.025	49.8	18.0	32.2	4.33	1.50	2.58	0.274	0.210
0.025 to 0.21	49.8	18.0	32.2	0.52	1.50	2.58	0.274	0.210
0.21 to 0.52	71.0	17.4	11.7	0.28	1.69	1.25	0.167	0.084
0.52 to 0.92	28.6	19.2	52.2	0.22	1.34	0.23	0.421	0.309
0.92 to 1.26	34.9	24.0	41.2	0.22	1.36	0.34	0.367	0.312

[a] The average was over five measurements for each soil horizon.
[b] OC: soil organic carbon content; ρ: bulk density; K_s^a: arithmetic mean of the measured saturated hydraulic conductivity; $\theta_{.33}$: soil water content at −33 kPa potential; and θ_{15}: soil water content at −1500 kPa potential.

courses. Therefore, the models were calibrated for CN_{II} using measured rainfall and run-off in 1994 by minimizing the differences between measured and simulated run-off. The optimized CN_{II} value was 83 for GLEAMS and PRZM-2. This value is within the range reported for pasture by USDA-SCS for hydrologic soil group C (from 74 to 86), suggesting that run-off curve numbers complied for pasture/rangeland vegetation[10] could be used as a first estimate for golf courses. This value was then applied to 1995 and 1996 for surface water run-off predictions.

Measured run-off of the diethylamine salt of 2,4-D was used to evaluate the GLEAMS and PRZM-2 models for pesticide run-off simulations from the golf course fairway. The decay rate of 2,4-D was 0.277 day^{-1} on foliage and 0.157 day^{-1} in soil, based on data collected for 'Tifwarf' bermudagrass.[9] The equilibrium sorption constant required by PRZM-2 was obtained from the batch adsorption experiment for each soil horizon (unpublished data). GLEAMS requires the normalized equilibrium sorption constant which is the partitioning coefficient between soil organic carbon and solution. This coefficient was calculated by dividing the measured equilibrium sorption constant by the soil organic carbon content of the horizon. For the top soil horizon, this value was 36.8.

GLEAMS can explicitly simulate pesticide injection application where the pesticide is injected into the user-specified depth without mixing with the soil above this depth. PRZM-2 does not have an option to allow for simulations of pesticide injection applications. The soil incorporation application method was used instead to simulate pesticide injection applications. The depth of incorporation was set equal to the injection depth in GLEAMS, which is 10 mm.

Parameter values for turf growth for GLEAMS and PRZM-2 were obtained from the database included in GLEAMS for bermudagrass. This database was built based on studies in Tifton, GA on the same variety of turf as that used in this study. Because of this and the similar environments between the two sites, the default parameter values in GLEAMS were used with minor modifications to adjust the differences in dates of turf emergence and maturity. The same parameter values were also applied to PRZM-2 for simulating turf growth and development.

3.3 Statistical analysis for goodness of fit

We used normalized root mean square error (NRMSE)[17] and least square linear regression fits of predicted versus observed run-off to quantify the accuracy of model simulations. The NRMSE is calculated by:

$$\mathrm{NRMSE} = \frac{100}{O_m}\sqrt{\frac{\sum_{i=1}^{n}(P_i - O_i)^2}{n}} \qquad (1)$$

where O_i is the observed value, O_m is the mean of the observed values, P_i is the corresponding predicted value, and n is the number of observations. The best-fit line is obtained by minimizing the sum of squares of deviations between observed and predicted data:

$$P_i = \beta O_i + \alpha + \varepsilon_i \qquad (2)$$

where α and β are intercept and slope of the best-fit line, respectively, and ε is an error term (unobserved error for pair data i). Good model simulations result in α not significantly different from zero (high precision) and β not significantly different from 1 (high accuracy), based on the t statistics. To ensure that good model fits are not just fortuitous, a scattergram and the coefficient of determination of the data are often accompanied by the regression analysis. When the normality assumption for α and β evaluations failed, the Mann–Whitney rank sum test was used instead to evaluate differences between measured and predicted values. All statistical analyses were performed at 0.05 significance level unless specified otherwise.

4 RESULTS AND DISCUSSION

4.1 Measured and simulated surface water run-off

Data in Fig 1 show the measured surface water run-off and those simulated by the GLEAMS and PRZM-2 models from 1994 to 1996. While in general the variability in measured run-off was large between plots, for clarity only the mean of measured run-off was shown, as the standard deviation would make it difficult to distinguish between measured and simulated run-off. The mean was calculated for each individual run-off event over measurements from the 12 plots. Compared with the mean of the measured water run-off, both model simulations

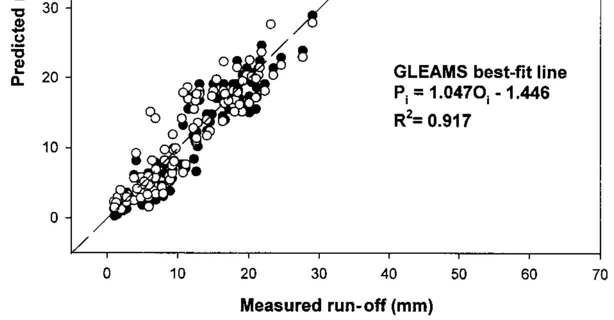

Figure 1. Measured and simulated surface water run-off by (●) GLEAMS and (○) PRZM-2 from 1994 to 1996.

were fairly accurate. The normalized root mean square error (NRMSE) for 1994, 1995 and 1996 was respectively 24.8, 23.9, and 21.2% for GLEAMS and 22.8, 27.2, and 24.2% for PRZM-2. The overall NRMSE for the three years was 22.8% for GLEAMS and 23.7% for PRZM-2, indicating that both models equally and adequately predicted surface water run-off.

To apply the linear regression analysis to measured and model-predicted run-off, we first examined the independence assumption on which this analysis is based. The correlogram of Fig 2 shows that no serial correlation existed among the residuals (predicted run-off minus measured run-off). We then proceeded to the linear regression fit of predicted and measured values, and subsequently added the results into Fig 1, which includes the coefficients of determination (R^2), the best-fit equations, and the line of perfect fit ($\alpha = 0$ and $\beta = 1$). A close examination of data in Fig 1 showed that the scatter of the points (measured versus predicted pairs) around the regression line did not tend to increase (or decrease) as the values of the measured run-off increased (or decreased), indicating that the variance of the residuals did not correlate with the independent variable (measured run-off). However, a normality test (Kolmogorov–Smirnov test) failed at 0.05 significance level for GLEAMS ($P \leq 0.001$) and PRZM-2 ($P \leq 0.001$). Therefore, the significance of α and β could not be rigorously evaluated based on the t statistic. We then applied the Mann–Whitney rank sum test, which demonstrated that difference between measured and model-predicted water run-off was not significant for either GLEAMS ($P = 0.151$) or PRZM-2 ($P = 0.587$). Graphically, the distribution of the data along the line of perfect fit (Fig 1) also indicates that GLEAMS and PRZM-2 reasonably simulated the average of measured surface water run-off over all plots.

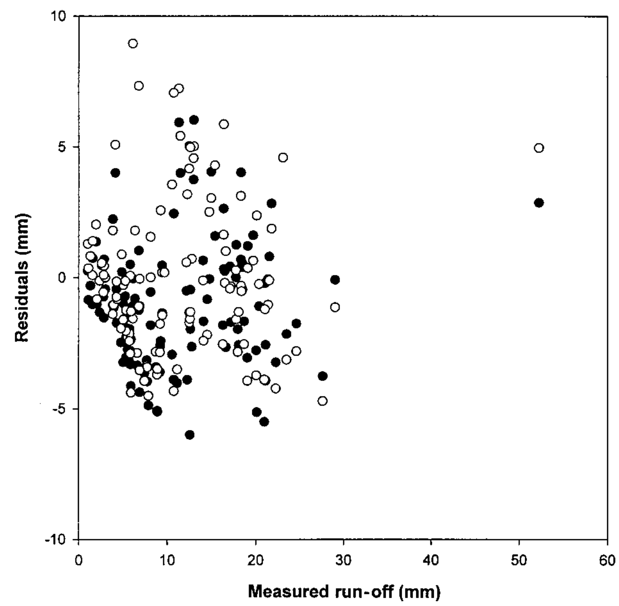

Figure 2. Distributions of residuals (predicted water run-off minus measured water run-off) in relation to measured surface water run-off. (●) GLEAMS (○) PRZM-2.

In applying an earlier version of PRZM-2 (PRZM) to surface water run-off predictions, Zacharias and Heatwole[18] reported that PRZM over-predicted surface water run-off by a factor of more than two. They found that over-predictions of water run-off were a result of under-predictions of evapotranspiration (ET). When using the potential ET calculated by GLEAMS as a direct input to PRZM, Zacharias and Heatwole again found that the model under-predicted actual ET and over-predicted water run-off. Although they did not describe whether or not the crop grew under water-stressed conditions, under-predictions of actual ET indicate that the crop probably grew under such conditions. In a recent application of PRZM-2 to surface water run-off predictions from a corn field under conventional tillage and water-stressed conditions, Ma *et al*[19] found that the model significantly over-predicted water run-off even after model calibrations using independently measured data. The over-predictions were shown to result from under-predictions of ET under water-stressed conditions.[19] Together, results from the previous studies and the present study suggest that PRZM-2 would reasonably predict surface water run-off under well-watered condition and over-predict run-off and under-predict ET under water-stressed conditions. As analyzed by Ma *et al*[19] over-predictions of run-off and under-predictions of ET by PRZM-2 under water-stressed conditions were related to the model internal constraints which over-reduce ET when soil water becomes limiting.

When predicted surface water run-off was compared with measured run-off from each individual plot over time (see the example shown in Fig 3 for plot-1 in 1994), the match was rather poor for either GLEAMS (NRMSE = 52.8%, $\alpha = -0.262$ mm, $\beta = 0.710$, $R^2 = 0.798$) or PRZM-2 (NRMSE = 52.6%, $\alpha = 1.211$ mm, $\beta = 0.647$, $R^2 = 0.741$). This should be expected because the model prediction should represent the average of the field conditions and the models were parameterized this way. Therefore, the model prediction should be compared with the average of the measurements over all plots. We used the arithmetic average to represent the data, assuming that the spatial variations of the hydrologic properties changed linearly. On the other hand, the spurious influences of random errors and events tended to be captured in each individual measurement, while collectively, these spurious influences might be reduced or even cancelled out by using an estimation (eg the arithmetic average) statistically summarized from all measurements. Comparisons between model simulations and very limited measurements (sometimes only one single measurement at a time) without considering the representativity of measured data can easily lead to biased judgements about the model performance, causing confusions in future model applications. We suggest that it is not

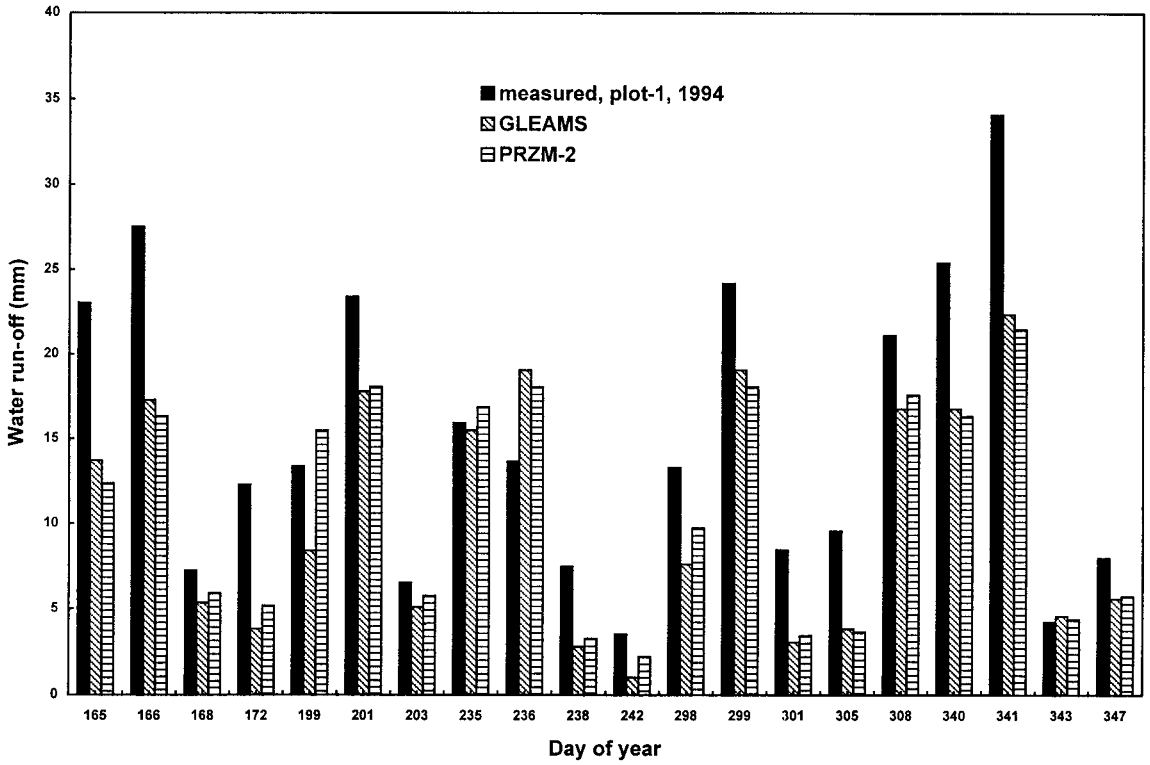

Figure 3. Measured and simulated surface water run-off by GLEAMS and PRZM-2 from plot-1 in 1994.

the individual measurement or point, but the representative measured data that should be compared with model simulations. The mixed success and failure as seen in the literature concerning a specific model in various applications may result from the uncertainties in measured data, even though the correctness of a model was often challenged whenever mis-matches occurred. These results indicate the importance of using representative data in model validation and performance comparison.

When predicted surface water run-off was compared with each measured run-off from all individual plots on a specific date (see the example shown in Fig 4 for day 168 in 1994), both model simulations were always within the range of the measurements, although GLEAMS predicted smaller run-off than did PRZM-2 on that day. Thus, we had difficulty in invalidating the models. In comparing the Opus model predictions with measured soil water content distributions across a 1.3-ha field, Smith and Ferreira[20] encountered the same problem. While it was shown that many combinations of model parameter values gave equally good (or poor) matches of model predictions with measurements as a result of model over-parameterization or lack of local parameter identification,[21,22] our study indicated that large spatial variability between plots overwhelmed the run-off process, making each individual run-off measurement lose its system representativity. Therefore, the problem might not be all with the model, but also with the complexity of the conditions and the quality and representativeness of measured data. Bias can only be reduced and avoided by using representative data in model validation and testing.

The above three levels of comparison suggest that adequate samples be taken to be representative of the field conditions in model validation and testing. However, in practice, the substantial costs that accompany increasing measurements often limit the number of samples taken. Burns *et al*[23] described means of computing the minimum number of samples required to ensure a model's validity concerning chemical risk analysis and hazard assessment.

One of the commonly recommended applications of simulation models is to test severe scenarios.[24] On 26 July 1996 (day 208), we applied 99.8 mm rainfall in 4 h to the plots to imitate two thunderstorms that occurred on 4 July (147.8 mm) and 5 July (177.0 mm) 1994 in this area. Such a rainfall occurred with a return frequency of approximately 10 years in the south-eastern USA, based on our analysis of 15-min rainfall records from 1985 to 1994. Run-off from these two storms was not measured because the whole area was flooded. Run-off from this simulated severe rainfall was 52.3 mm as measured, 55.12 mm as predicted by GLEAMS and 57.21 mm by PRZM-2. The relative errors of 5.4% for GLEAMS and 9.4% for PRZM-2 indicate that both models adequately predicted the amount of run-off from this extremely heavy rainfall.

4.2 Measured and simulated surface transport of 2,4-D

Data in Fig 5 are used to show the measured and predicted surface run-off of 2,4-D by GLEAMS and PRZM-2 in 1994. The mean of measured 2,4-D concentrations and its standard error were both shown.

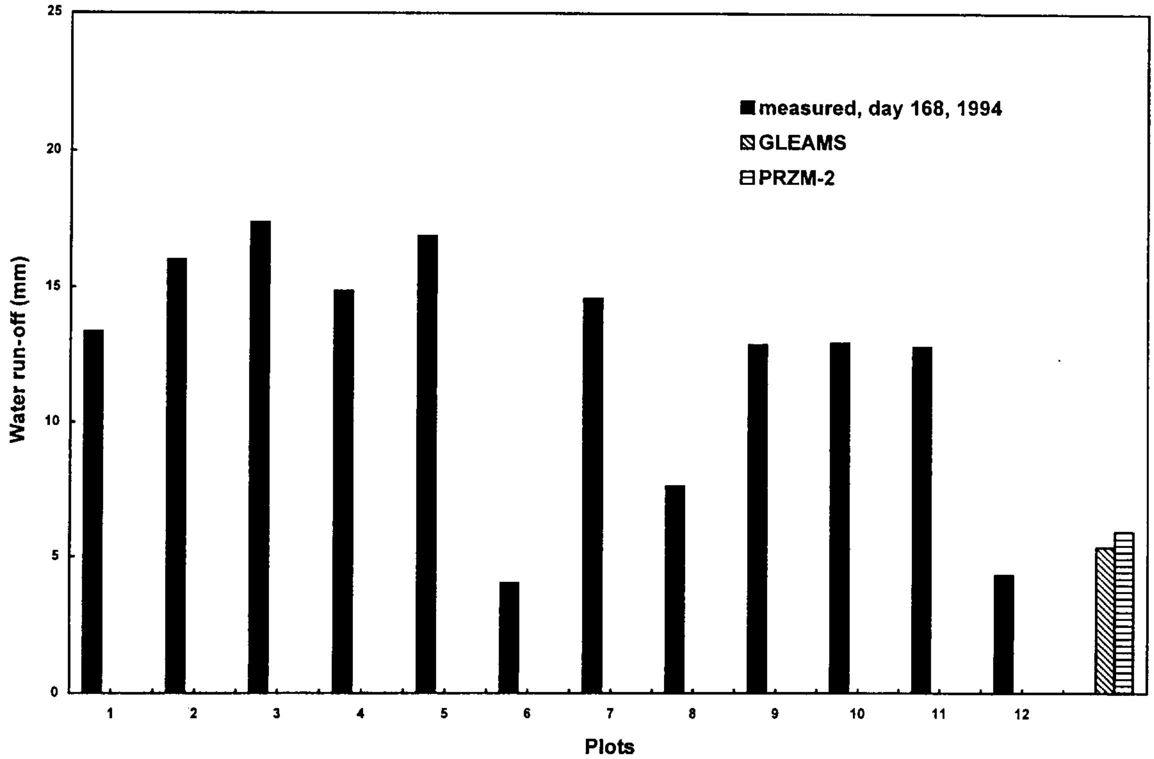

Figure 4. Measured and simulated surface water run-off by GLEAMS and PRZM-2 from the 12 plots on day 199 in 1994.

The mean was calculated for each run-off event over the plots in which the measurements were made. Those for 1995 and 1996 generally followed the pattern of 1994 except for pressure injection applications and for foliar applications to sparse canopy, for which model simulations differed greatly from measurements. These exceptions are described in more detail below.

The average of 2,4-D run-off from all the first post-treatment run-off events during the three years of studies was 6.8% of applied 2,4-D. Even in summer, 2,4-D run-off from the first post-treatment

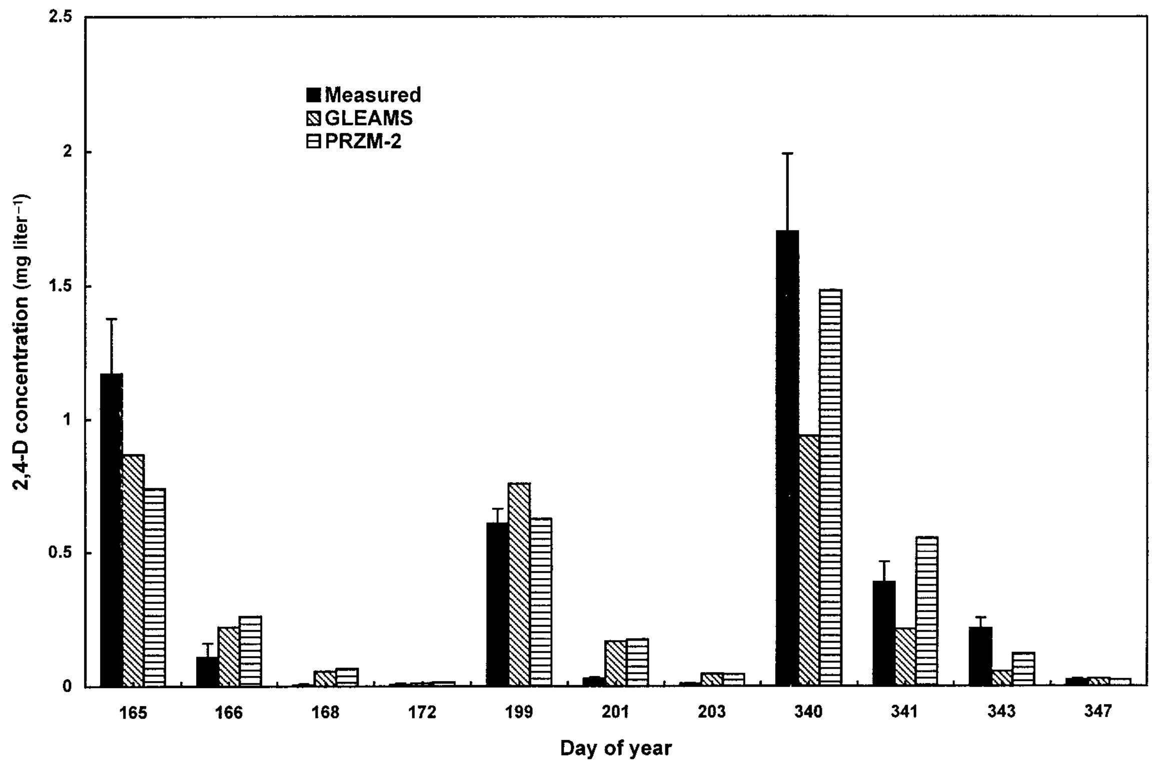

Figure 5. Measured (with error bars) and simulated 2,4-D concentrations in run-off by GLEAMS and PRZM-2 in 1994.

run-off events averaged 6.0% of applied 2,4-D. The average of annual 2,4-D run-off from all run-off events was 9.1% of applied 2,4-D. A calculation based on these data reveals that 74.5% of the total 2,4-D run-off occurred in the first post-treatment run-off events, indicating that the quantity of the pesticide available for surface run-off decreased rapidly and that golf course management should focus on these critical events to protect water quality.

Surface run-off of pesticides from agricultural fields is generally less than 5% of the application rate on seasonal or annual basis.[1,25] Compared with this percentage, 2,4-D run-off percentage observed in this study was relatively high, suggesting that the potential impacts of pesticide run-off from urban systems such as golf courses cannot be overlooked. This percentage is, however, a result of the severe scenarios used in this study. It is also a result of the high water solubility and low adsorption of the pesticide. In a parallel study on surface run-off of chlorpyrifos (O,O-diethyl O-(3,5,6-trichloro-2-pyridyl) phosphorothioate) and chlorothalonil (2,4,5,6-tetrachloro-1,3-benzenedicarbonitrile) from these plots under the same conditions, we found that the average percentage transported via the first post-treatment run-off events was only 0.000 19% and 0.17% of applied chlorpyrifos and chlorothalonil, respectively. These two pesticides have much lower water solubility and greater adsorption than 2,4-D, based on measurements in our laboratory (unpublished data). In addition, high rainfall intensity used here enhanced the mixing between raindrops and soil solution, making more chemicals available for surface run-off. The low saturated hydraulic conductivity of the Cecil sandy clay loam further contributed to the large quantity of the pesticide transported via surface run-off. These results demonstrate that surface transport of pesticides depends heavily on their intrinsic properties and also on the environmental conditions. Since 2,4-D has similar water solubility and relatively higher adsorption capacity than nitrate fertilizers, the run-off potential of the fertilizers under such conditions is well worthy of study because of the various potential health problems with the nitrate fertilizers.

These results suggest that pesticide intrinsic properties such as water solubility, sorption and persistence, as well as external conditions, including soil properties, land uses, antecedent soil moisture conditions and climatic conditions must all be considered in pesticide use decision-making. Note that run-off was measured at the edge of the plot (or field), while in practice, there usually exists a buffer zone between pesticide application areas and surface water resources, which could reduce pesticide concentrations in run-off via various dilutions and filtrations.[26] These results were obtained from field plots, and scale differences in hydrologic responses between field plots and typical larger fields could influence the amount of pesticides in run-off. Wauchope[1] showed that surface transport of pesticides from small plots could be over-estimated by a factor up to two compared with that from typical larger fields.

Quantitative predictions of pesticide run-off are by using simulation models such as GLEAMS and PRZM-2 in which major influencing processes are quantified and integrated. Data in Fig 5 show that neither GLEAMS nor PRZM-2 accurately simulated 2,4-D concentrations in run-off from the plots, especially at relatively low or high concentrations. The NRMSE for 1994, 1995 and 1996 was respectively 112.8, 108.5, and 57.7% for GLEAMS and 71.9, 118.7, and 138.5% for PRZM-2. The overall NRMSE for all data was 82.1% for GLEAMS and 125.8% for PRZM-2, again indicating that neither model accurately simulated 2,4-D run-off overall.

For the two pressure injection applications which occurred in August 1995 and in September 1996, GLEAMS significantly under-predicted the concentrations of 2,4-D in run-off ($P < 0.001$), while PRZM-2 predicted even lower concentrations. The under-predictions of 2,4-D concentrations in run-off indicate that neither model accurately simulated transfer of the pesticide into surface run-off. For the foliar applications before significant canopy was developed in January and February 1996, GLEAMS reasonably predicted 2,4-D concentrations for the first post-treatment run-off events but under-predicted the concentrations for all other run-off events. In contrast, PRZM-2 significantly under-predicted 2,4-D concentrations for all run-off events ($P < 0.001$). Better simulations were achieved for GLEAMS because the model allows users to specify partitioning of applied pesticides between foliage and soil surface. The under-prediction of 2,4-D concentrations in run-off by PRZM-2 was a result of the incorrect partitioning of applied 2,4-D between canopy and soil surface due to an inaccurate simulation of the soil surface cover.

Distinct differences exist in surface cover conditions between an agricultural system and a golf course. For agricultural fields under conventional management practices, soil surface is generally fallow or lightly covered by residues before planting or after harvest. For golf courses, soil surface is almost always covered by canopy, whether it is growing turf or dry standing matter, even before and after turf growth period. Standing grasses could effectively intercept and retain applied pesticides. Therefore, for golf courses, the majority of the foliage spray presumably did not immediately reach the soil surface at any time during the application. Instead, it was first intercepted by grass canopy and then washed off the canopy by subsequent rainfall. The fraction of the pesticide that was gradually washed off the foliage could be directly available for run-off. The crop/turf growth model in PRZM-2 linearly develops a crop and canopy starting from emergence, therefore, PRZM-2 partitioned most of applied pesticide to soil

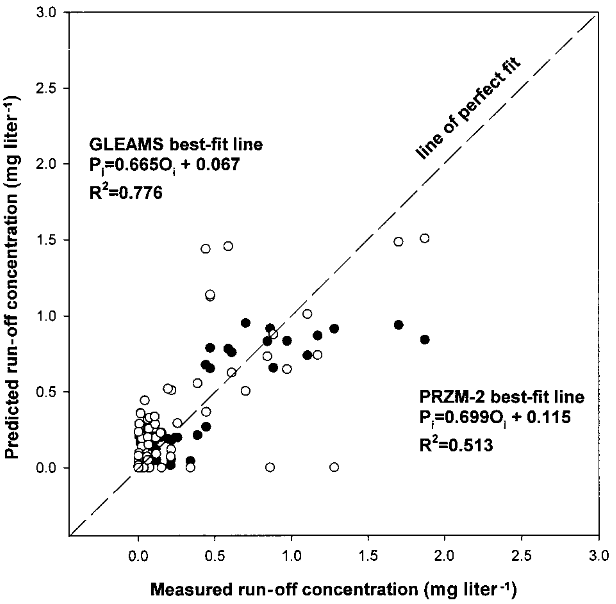

Figure 6. Linear regression analyses of measured and simulated 2,4-D concentrations in run-off by (●) GLEAMS and (○) PRZM-2 from 1994 to 1996.

surface before emergence or at early grass growth stages. As described previously, PRZM-2 significantly under-predicted surface run-off of 2,4-D when it was applied directly on soil surface; as a result, the model also under-predicted surface run-off of 2,4-D for those foliar applications for which the model did not correctly partition applied 2,4-D between foliage and soil surface. The larger NRMSE for PRZM-2 predictions was caused mainly by run-off simulations for these run-off events. This problem is corrected in the newest version, PRZM-3[27] in which more options are provided for applying pesticides and partitioning applied pesticides between foliage and soil surface. With these corrections, we expect that PRZM-3 would better predict 2,4-D run-off.

Another source of errors is the inability of the models to simulate multi-rainfall events that occur in the same day. These events have a significant effect on surface run-off of pesticides such as 2,4-D which has a high water solubility and low sorption. For example, on 17 July 1995, 2,4-D was applied as foliar spray. Two hours before the simulated rainfall was applied, a 5.6-mm natural rainfall occurred. It did not generate measurable surface water run-off, but clearly it washed off a fraction of applied pesticide from foliage and leached this fraction into the soil profile. The quantity of 2,4-D measured from the simulated rainfall/run-off event that followed was significantly smaller than that measured from previous run-off events without a pre-event rainfall. Since GLEAMS and PRZM-2 operate on a daily time-step, they are not able to separate these two rainfall events. As a result, the models predicted more instead of less 2,4-D in the first post-treatment run-off event, more because the models assumed that the two rainfalls were combined producing more water run-off.

A linear regression analysis between measured and GLEAMS-predicted 2,4-D concentrations in surface water run-off for all data (Fig 6) showed that the model significantly under-predicted surface run-off

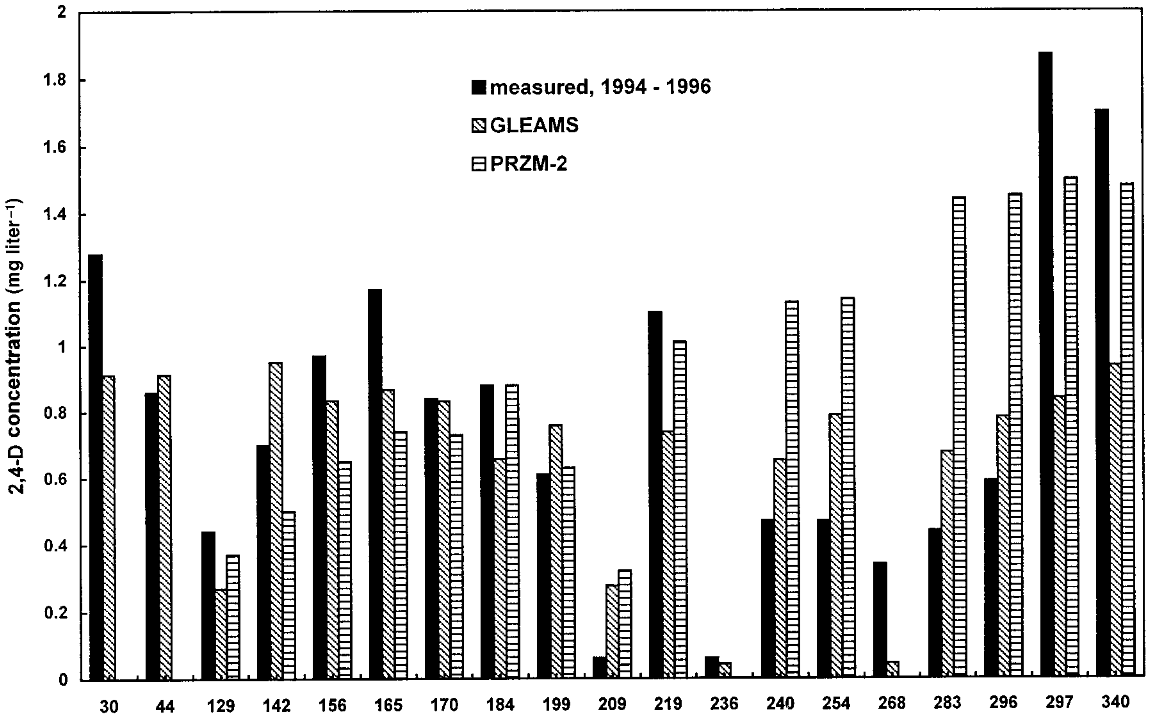

Figure 7. Measured and simulated 2,4-D concentrations in run-off from all the first post-treatment events by GLEAMS and PRZM-2 from 1994 to 1996.

of 2,4-D at high concentrations. A similar analysis for PRZM-2 was also included in Fig 6. A close examination of the data in Fig 6 for PRZM-2 simulations demonstrated that the model generally over-predicted 2,4-D concentrations in run-off when concentrations were low and under-predicted 2,4-D concentrations when concentrations were high. Overall, both GLEAMS ($\alpha = 0.067$ mg liter^{-1}, $\beta = 0.665$, $R^2 = 0.776$) and PRZM-2 ($\alpha = 0.115$ mg liter^{-1}, $\beta = 0.699$, $R^2 = 0.513$) under-predicted 2,4-D concentrations in run-off.

Surface run-off of pesticides from the first post-treatment run-off events is almost always critical in determining potential impacts of run-off pesticides on surface water quality.[1] Data in Fig 7 show measured and simulated 2,4-D concentrations in run-off by GLEAMS and PRZM-2 for all the first post-treatment run-off events during the study. Of the total 19 such critical events, 16 were simulated within a factor of two of the measured run-off concentrations by GLEAMS and 10 by PRZM-2. As discussed previously, PRZM-2 did not adequately simulate 2,4-D concentrations in run-off for pressure injection applications and for foliar applications to sparsely covered canopy, and such events occurred in four out of the nine from which simulated concentrations differed from measurements by a factor of more than two. For GLEAMS, there was one pressure injection application for which simulated 2,4-D concentrations in run-off from critical events were more than two-fold off from the measurements. These results indicate that, overall, neither GLEAMS nor PRZM-2 adequately predicted 2,4-D concentrations in surface water run-off from critical events based on the commonly accepted criteria.[28]

5 CONCLUSIONS

Three years of field studies on run-off potential of the diethylamine salt of 2,4-D from a golf course fairway demonstrated that concentrations of the pesticide via surface water run-off decreased rapidly, with the first post-treatment event run-off averaging 74.5% of the total 2,4-D run-off. Significant amounts of foliage-applied 2,4-D transported via surface run-off were a result of the severe scenarios used in this study; on the other hand, it reflects run-off potential of this water-soluble pesticide under the intensive management practices of a typical golf course. Applications of the GLEAMS and PRZM-2 models showed that both models adequately simulated surface water run-off, but when applied for predicting 2,4-D concentrations in surface run-off, the simulations were less accurate. Significant differences between measured and PRZM-2-predicted 2,4-D concentrations in run-off were mainly caused by inaccurate partitioning of applied 2,4-D between soil surface and turf canopy. This study re-emphasizes that potential impacts of the intensive uses of pesticides in urban systems such as golf courses cannot be overlooked.

ACKNOWLEDGEMENTS

We thank Mr Nehru Mantriprogada and Mr Hal Peeler of the Department of Crop and Soil Sciences, University of Georgia for pesticide residue analysis and Ms Dee Dee Gresham of the Department of Agricultural Engineering, University of Georgia for sharing the weather data. We are also indebted to Dr R Don Wauchope for considerable help in clarifying the material.

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